

# PM<sub>2.5</sub> and PM<sub>10</sub> Mass Measurements in California's San Joaquin Valley

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PM<sub>2.5</sub> and PM<sub>10</sub> mass measurements from different sampling systems and locations within California's San Joaquin Valley (SJV) are compared to determine how well mass concentrations from a unified data set can be used to address issues such as compliance with particulate matter (PM) standards, temporal and spatial variations, and model predictions. Pairwise comparisons were conducted among 20 samplers, including four Federal Reference Method (FRM) units, battery-powered MiniVols, sequential filter samplers, dichotomous samplers, Micro-Orifice Uniform Deposit Impactors (MOUDIs), beta attenuation monitors (BAMs), tapered element oscillating microbalances (TEOMs), and nephelometers. The differences between FRM samplers were less than 10 and 20% for 70 and 92% of the pairwise comparisons, respectively. The TEOM, operating at 50°C in this study, measured less than the other samplers, consistent with other comparisons in nitrate-rich atmospheres. PM<sub>2.5</sub> mass measured continuously with the BAM was highly correlated with filter-based PM<sub>2.5</sub> although the absolute bias was greater than 20% in 45% of the cases. Light scattering ( $B_{sp}$ ) was also highly correlated with filter-based PM<sub>2.5</sub> at most sites, with mass scattering efficiencies varying by 10 and 20% for  $B_{sp}$  measured with Radiance Research nephelometers with and without PM<sub>2.5</sub> size-selective inlets, respectively. Collocating continuous monitors with filter samplers was shown to be useful for evaluating short-term variability and identifying outliers in the filter-based measurements. Comparability among different PM samplers used in CRPAQS is sufficient to evaluate spatial gradients larger than about 15% when the data are pooled together for spatial and temporal analysis and comparison with models.

## INTRODUCTION

Particulate Federal Reference Methods (FRMs) are intended to determine compliance with U.S. National Ambient Air

Quality Standards (NAAQS) for PM<sub>10</sub> (U.S. EPA 1987) and PM<sub>2.5</sub> (U.S. EPA 1997a). U.S. Environmental Protection Agency (U.S. EPA) NAAQS for PM<sub>10</sub> are 50 and 150  $\mu\text{g}/\text{m}^3$  for annual arithmetic and 24-h average concentrations, respectively. Twenty-four hour PM<sub>10</sub> concentrations are rounded to the nearest 10  $\mu\text{g}/\text{m}^3$  to determine compliance. The annual arithmetic average NAAQS for PM<sub>2.5</sub> is 15  $\mu\text{g}/\text{m}^3$  averaged over three years and rounded to the nearest 1  $\mu\text{g}/\text{m}^3$ . U.S. EPA (1997a) provides for spatial averages of neighborhood-scale or urban-scale monitors (Chow et al. 2002). The 24-h average NAAQS is 65  $\mu\text{g}/\text{m}^3$  evaluated from the three-year average of the 98th percentile of 24-h concentrations, with rounding to the nearest 1  $\mu\text{g}/\text{m}^3$ . The State of California annual standards for PM<sub>2.5</sub> and PM<sub>10</sub> are 12 and 20  $\mu\text{g}/\text{m}^3$ , respectively, and a 24-h average PM<sub>10</sub> standard of 50  $\mu\text{g}/\text{m}^3$  (California Air Resources Board 2002).

FRM sampler characteristics and operating procedures for PM<sub>2.5</sub> and PM<sub>10</sub> compliance monitoring are highly specified (U.S. EPA 1997b) to assure uniformity among mass measurements across the entire United States. However, these specifications are not compatible with the need to understand the causes of elevated PM<sub>2.5</sub> and PM<sub>10</sub>. Such understanding often requires the use of non-FRM methods with various size-selective inlets, sampler materials, filter media, and filter handling procedures to accommodate different time scales (other than 24 hours) and chemical analyses (Chow 1995). FRMs and Federal Equivalent Methods (FEMs) sometimes underestimate PM<sub>2.5</sub> and PM<sub>10</sub> mass owing to volatilization of ammonium nitrate ( $\text{NH}_4\text{NO}_3$ ; Chow et al. 2005) and organic carbon (Pang et al. 2002; Chow et al. 2006), and sometimes overestimate these quantities owing to differences in inlet sampling effectiveness (Watson et al. 1993; Wedding and Carney 1983), adsorption of gases by the filter media (Keck and Wittmaack 2005), and differences in filter processing environments (Hanninen et al. 2002). Studies using FRMs and more-versatile PM samplers to describe PM<sub>2.5</sub> and PM<sub>10</sub> spatial and temporal variations must establish comparability among those samplers. The purpose of this analysis is to evaluate that comparability for the California Regional PM<sub>10</sub>/PM<sub>2.5</sub> Air Quality Study (CRPAQS), a major effort to understand the

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TABLE 1

Summary of PM<sub>2.5</sub> and PM<sub>10</sub> sampling locations during the California Regional PM<sub>10</sub>/PM<sub>2.5</sub> Air Quality Study (CRPAQS)

Station	Code	Address	Network_code	Latitude (north)	Longitude (west)	Elev. (m) <sup>g</sup>
Angiola	ANGI <sup>a</sup>	36078 4th Ave.	CRPAQS <sup>c</sup>	35° 56' 53"	119° 32' 16"	60
Bakersfield	BAC <sup>a</sup>	5558 California Ave.	CRPAQS/ARB <sup>d</sup>	35° 21' 24"	119° 3' 45"	119
Bethel Island	BTI <sup>a</sup>	5551 Bethel Island Rd.	CRPAQS/BAQ <sup>e</sup>	38°0'23"	121° 38' 31"	2
Fresno Supersite	FSF <sup>a</sup>	3425 N 1st St.	CRPAQS/ARB	36° 46' 54"	119° 46' 24"	97
Sierra Nevada Foothills	SNFH <sup>a</sup>	31955 Auberry Rd.	CRPAQS	37° 3' 45"	119° 29' 46"	589
Corcoran	COP <sup>b</sup>	1520 Patterson Ave.	SJV <sup>f</sup>	36° 6' 8"	119° 33' 57"	63
Livermore	LVR <sup>b</sup>	793 Rincon St.	CRPAQS	37° 41' 15"	121° 47' 3"	138
Modesto	M14 <sup>b</sup>	814 14th St.	ARB	37° 38' 31"	120° 59' 40"	28
Sacramento	S13 <sup>b</sup>	1309 T St.	ARB	38° 34' 6"	121° 29' 36"	6
San Jose	SJ4 <sup>b</sup>	120 N. 4th St.	CRPAQS/BAQ	37° 20' 23"	121° 53' 19"	26
Stockton	SOH <sup>b</sup>	1601 E. Hazelton Rd.	ARB	37°57'1"	121° 16' 8"	8
Visalia	VCS <sup>b</sup>	310 N Church St.	ARB	36° 19' 57"	119° 17' 28"	102

<sup>a</sup>Anchor sites.<sup>b</sup>Selected satellite sites.<sup>c</sup>As part of the California Regional PM<sub>10</sub>/PM<sub>2.5</sub> Air Quality Study.<sup>d</sup>Operated by the California Air Resources Board.<sup>e</sup>Operated by the Bay Area Air Quality Management District.<sup>f</sup>Operated by the San Joaquin Valley Air Quality Management District.<sup>g</sup>Meters above mean sea level (MSL).

NAAQS exceedances in California's San Joaquin Valley (SJV, Watson et al. 1998). This evaluation is necessary because PM<sub>2.5</sub> and PM<sub>10</sub> from several different samplers are being used to verify chemical mass closure, determine spatial gradients, estimate source contributions, refine conceptual models, and evaluate the performance of source-oriented air quality models.

The 14-month-long CRPAQS was conducted in central California from December 2, 1999 through February 3, 2001 to determine the causes of elevated levels of PM<sub>2.5</sub> and PM<sub>10</sub> and to evaluate the means of reducing them with respect to federal and state air quality regulations. The Fresno Supersite (Watson et al. 2000), which operated concurrently with the CRPAQS, offered an opportunity to compare many of the CRPAQS sampling systems with FRMs. Measurements from these instruments were further supplemented with those of monitors at other state and local air monitoring stations in central California.

Previous studies comparing PM<sub>2.5</sub> and PM<sub>10</sub> mass concentrations from FRM samplers and other integrated filter-based and continuous monitors (Tropp et al. 1998; Chang et al. 2001; Chung et al. 2001; Peters et al. 2001; Poor et al. 2002; Watson and Chow 2002; Motallebi et al. 2003; Solomon et al. 2003; Charron et al. 2004; Lee et al. 2005), show that monitors are comparable when the particles are small (mostly <2.5  $\mu\text{m}$ ) and the aerosol is chemically stable (e.g., dominated by ammonium sulfate). Poorer comparability is found when the aerosol is volatile (e.g., dominated by NH<sub>4</sub>NO<sub>3</sub>) and when particles with diameters similar to the sampling inlet cut-point are abundant (e.g., fugitive dust). SJV aerosol presents a challenging test because it is high in nitrate (NO<sub>3</sub><sup>-</sup>) during the fall and winter, and often experiences fugitive dust components during non-winter months.

## METHODS

Aerosol sampling for the CRPAQS and at the Fresno Supersite (FSF) was conducted for an annual campaign and for fall and winter intensive operating periods (IOPs) at five anchor sites: two urban-scale sites at FSF and Bakersfield (BAC), two regional-scale inter-basin boundary sites at Bethel Island (BTI) and Sierra Nevada Foothills (SNFH), and one regional-scale intra-basin site at Angiola (ANGI). Desert Research Institute (DRI, Reno, NV) sequential filter samplers (SFS) were operated at all five locations. The annual sampling campaign included 24-h (midnight-to-midnight) samples collected on the U.S. EPA every-sixth-day schedule starting on 12/2/99 at FSF, BAC, and ANGI, and on 12/2/00 at BTI and SNFH, ending on 2/3/01. The fall IOP included daily 24-h samples collected at FSF and ANGI on the following 17 days: 10/14/00, 10/16/00 to 10/20/00, 10/22/00 to 10/24/00, and 11/2/00 to 11/9/00. The winter IOP included samples collected five times per day (0000–0005, 0005–1000, 1000–1300, 1300–1600, and 1600–2400 Pacific Standard Time [PST]) at five anchor sites on the following 15 days: 12/15/00 to 12/18/00, 12/26/00 to 12/28/00, 1/4/01 to 1/7/01, and 1/31/01 to 2/3/01. Size-segregated Micro-Orifice Uniform Deposit Impactor (MOUDI) samples were collected during the winter IOP at FSF and ANGI. PM<sub>2.5</sub> MOUDI concentrations were estimated from the sum of the masses on stages below (smaller than) the 2.5  $\mu\text{m}$  stage, including 2.5  $\mu\text{m}$  and after-filter stages.

For the annual sampling campaign, portable battery-powered PM<sub>2.5</sub> and PM<sub>10</sub> MiniVol samplers (Airmetrics, Eugene, OR) operated on the U.S. EPA every-sixth-day schedule at 35 PM<sub>2.5</sub> sites between 12/2/99 and 2/3/01. During the fall IOP,

TABLE 2  
Description of PM<sub>2.5</sub> and PM<sub>10</sub> samplers\*

Sampler code	Model	Manufacturer <sup>a</sup>	Size	FRM <sup>b</sup>	FEM <sup>c</sup>	Measurement principle
AN100	RAAS 100	Andersen	PM <sub>2.5</sub>	Yes	—	Gravimetric
AN300	RAAS300	Andersen	PM <sub>2.5</sub>	Yes	—	Gravimetric
RP2K	R&P 2000	Rupprecht & Patashnick	PM <sub>2.5</sub>	Yes	—	Gravimetric
RP225	R&P 2025	Rupprecht & Patashnick	PM <sub>2.5</sub>	Yes	—	Gravimetric
AN400	RAAS 400	Andersen	PM <sub>2.5</sub>	No	No	Gravimetric
M1ST	SASS speciation sampler	Met One	PM <sub>2.5</sub>	No	No	Gravimetric
DICHOTF	SA-246B	Andersen	PM <sub>2.5</sub>	No	No	Gravimetric
SFS	Sequential filter sampler	DRI	PM <sub>2.5</sub>	No	No	Gravimetric
MINIVOL25	MiniVol Portable	Airmetrics	PM <sub>2.5</sub>	No	No	Gravimetric
MOUDI	Model 100	MSP	PM <sub>2.5</sub>	No	No	Gravimetric
BAM25	BAM 1020	Met One	PM <sub>2.5</sub>	No	No	Beta Attenuation
TEOM25	TEOM 1400a	Rupprecht & Patashnick	PM <sub>2.5</sub>	No	No	Inertial Mass
DUSTTRAK	DustTrak 8520	TSI	PM <sub>2.5</sub>	No	No	Light Scattering
GREENTEK	GT640A	GreenTek	PM <sub>2.5</sub>	No	No	Light Scattering
RAD25	M903 (nephelometer)	Radiance Research	PM <sub>2.5</sub>	—	—	Light Scattering
RAD	M903 (nephelometer)	Radiance Research	TSP	—	—	Light Scattering
HIVOLIOV	GMW-1200	Andersen	PM <sub>10</sub>	Yes	—	Gravimetric
MINIVOL10	MiniVol Portable	Airmetrics	PM <sub>10</sub>	No	No	Gravimetric
BAM10	BAM 1020	Met One	PM <sub>10</sub>	No	Yes	Beta Attenuation
TEOM10	TEOM 1400a	Rupprecht & Patashnick	PM <sub>10</sub>	No	Yes	Inertial Mass

<sup>a</sup> Andersen Instruments (Thermo Electron, Waltham, MA); Rupprecht & Patashnick (now Thermo Electron, Albany, NY); Met One Instruments (Grants Pass, OR); Desert Research Institute (DRI, Reno, NV); Airmetrics (Eugene, OR); MSP Corporation (Minneapolis, MN); TSI, Inc. (Shoreview, MN); GreenTek (Atlanta, GA); Radiance Research (Seattle, WA).

<sup>b</sup> Federal Reference Method (U.S. EPA 1997).

<sup>c</sup> Federal Equivalent Method (Code of Federal Regulations 1988).

\*Data available at <http://www.arb.gov/airways/and> <http://www.arb.ca.gov/aqdcddld.htm>

PM<sub>10</sub> MiniVols sampled daily at 11 sites between 10/9/00 and 11/14/00. During the winter IOP, PM<sub>2.5</sub> MiniVol samples were collected daily at 25 sites from 12/15/00 to 12/18/00, 12/25/00, 12/27/00, 12/28/00, 1/4/01 to 1/6/01, and 2/1/01 to 2/3/01. These inexpensive sampling platforms require no formal infrastructure and allowed for a much larger spatial deployment than would have been possible using fixed-site samplers.

The five anchor sites and seven satellite sites—Corcoran (COP), Livermore (LVR1), Modesto (M14), Sacramento (S13), San Jose (SJ4), Stockton (SOH), and Visalia (VCS)—were used in the comparisons reported in this paper, shown in Figure 1, and described in Table 1. This data set contains: 24-h average and sub-daily, filter-based PM<sub>2.5</sub> and PM<sub>10</sub> concentrations; hourly mass measurements by beta attenuation monitor (BAM) (Met One Instruments, Grants Pass, OR) and tapered element oscillating microbalance (TEOM) (Rupprecht and Patashnick, Albany, NY); hourly mass measurements by photometers that convert forward light scattering to mass with internal scattering efficiency (DustTrak, Atlanta, GA; TSI, Inc., Shoreview, MN; and GreenTek, Atlanta, GA); and 5-minute particle light scattering (B<sub>sp</sub>) measurements by one nephelometer with no inlet (i.e., total

suspended particles [TSP]) and one with a PM<sub>2.5</sub> inlet (Radiance Research, Seattle, WA). The Radiance Research M903 nephelometer is equipped with a smart heater in which the airstream is heated when relative humidity (RH) exceeds ~65% to minimize the enhancement of B<sub>sp</sub> by hygroscopic growth; thus, it provides an approximate measure of dry B<sub>sp</sub>. Chow et al. (2001) described the relationship between B<sub>sp</sub> and PM<sub>2.5</sub> at sites in the western U.S. and Mexico.

The 20 samplers used for the comparison are listed by their code names in Table 2. For continuous monitors, only averages representing at least 18 hours (75%) per day were considered. Samplers were compared in pairwise (Y versus X) fashion. The “X” variable represents a benchmark, selected as an FRM when available, and the “Y” variable represents the comparison sampler.

Comparability was evaluated by using the following metrics (Watson and Chow 2002): (1) Ordinary least-squares (unweighted) regression (OL) of Y on X, resulting in a slope, intercept, and squared correlation (R<sup>2</sup>). FRM comparability specifications for slope, intercept, and R<sup>2</sup> are  $1 \pm 0.1$ ,  $0 \pm 5 \mu\text{g}/\text{m}^3$  and 0.94, respectively, for PM<sub>10</sub> samplers and  $1 \pm 0.05$ ,  $0 \pm 1 \mu\text{g}/\text{m}^3$

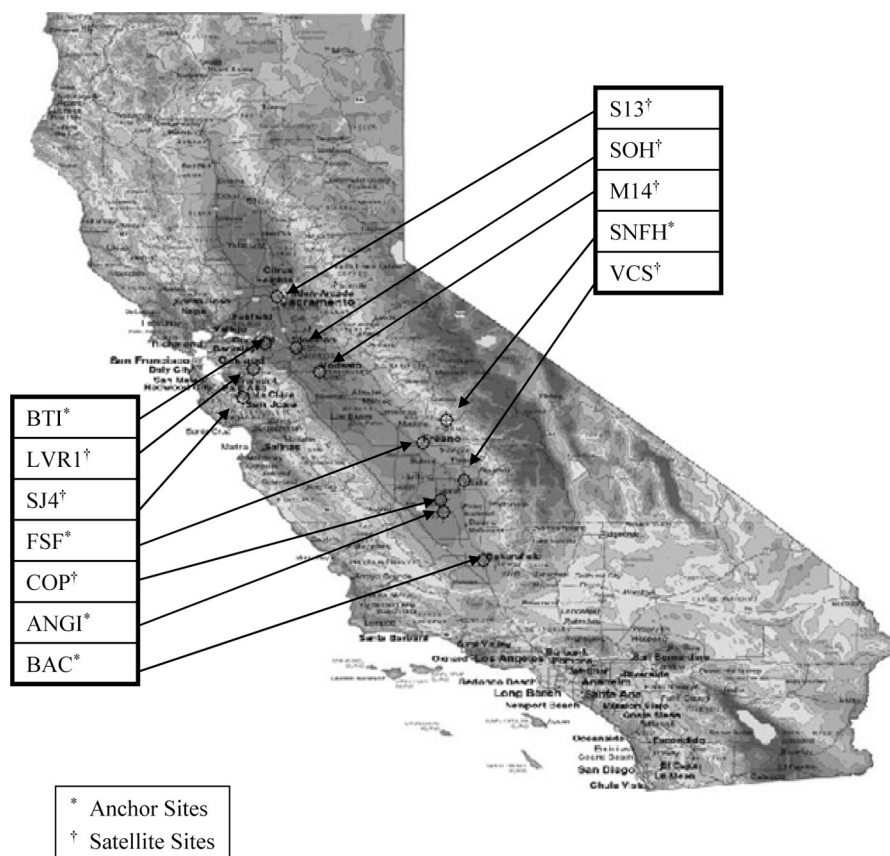


FIG. 1. Locations of the subset of CRPAQS anchor and satellite sites for PM<sub>2.5</sub> and PM<sub>10</sub> comparisons (see site codes in Table 1).

and 0.94, respectively, for PM<sub>2.5</sub> samplers (U.S. EPA 1997b); (2) Average ratio and standard deviation of  $Y/X$ ; (3) Distribution of  $Y - X$  with respect to its measurement uncertainty ( $\sigma_{Y-X}$ ); (4) Average difference between  $Y$  and  $X$  ( $\bar{Y} - \bar{X}$ ); (5) Standard deviation of  $\bar{Y} - \bar{X}$ ; (6) Measurement uncertainty of  $\bar{Y} - \bar{X}$ , also known as the root-mean square error (RMSE), defined as:

$$\text{RMSE} = \left[ \frac{1}{N} \sum_{i=1}^N (Y - X)^2 \right]^{1/2} \quad [1]$$

(7) A paired-difference T-test to evaluate the difference between  $Y$  and  $X$ .  $T$  is  $\bar{Y} - \bar{X}$  divided by its standard error (standard deviation of  $\bar{Y} - \bar{X}$  divided by the square root of the number of pairs). For sample sizes ( $N$ )  $> 30$ ,  $|T| > 1.96$  and significance probability ( $P$ )  $< 0.05$  implies that the difference between  $Y$  and  $X$  is significant; and (8) the average error (AE), between  $Y$  and  $X$ , expressed as a percentage, defined as:

$$\text{AE} = 100 \frac{1}{N} \sum_{i=1}^N \frac{Y_i - X_i}{X_i} \quad [2]$$

where  $i$  refers to the  $i$ th data pair and  $N$  is the number of pairs. This defines the average difference of  $Y$  with respect to  $X$ .

While it is instructive to compare  $Y - X$  with its measurement uncertainty, such uncertainties are available only for SFS, PM<sub>2.5</sub> and PM<sub>10</sub> MiniVol (MINIVOL25 and MINIVOL10), and PM<sub>2.5</sub> MOUDI measurements at the CRPAQS sites, and for PM<sub>2.5</sub> Andersen RAAS 100 (AN100) and RAAS 400 (AN400) measurements at the Fresno Supersite. The uncertainty ( $\sigma_C$ ) of an individual filter-based mass concentration ( $C$ ) is calculated from: (1) the uncertainty ( $\sigma_V$ ) of the sample volume, based on flow rate performance tests; (2) replicate precision ( $\sigma_F$ ) of the non-blank-corrected gravimetric mass ( $F$ ); and (3) the uncertainty ( $\sigma_B$ ) of the dynamic field blank ( $B$ ), which is the larger of the standard deviation of the individual blank values or their root-mean-squared analytical uncertainty as:

$$\sigma_C = [\sigma_V^2(F - B)^2/V^4 + (\sigma_F^2 + \sigma_B^2)/V^2]^{1/2} \quad [3]$$

In cases where uncertainties were available for only one sampler, it was assumed that the concentrations for the other sampler had the same uncertainties. The measurement uncertainty of  $Y_i - X_i$  (i.e.,  $\sigma_{Y_i - X_i}$ ) is the square root of  $\sigma_{Y_i}^2 + \sigma_{X_i}^2$ , where  $\sigma_{Y_i}$  and  $\sigma_{X_i}$  are the measurement uncertainties of  $Y_i$  and  $X_i$ , respectively.

TABLE 3  
Sampler comparison at the Fresno Supersite

Sampler <sup>d</sup>		Ordinary least squares <sup>b</sup> (μg/m <sup>3</sup> )		Correlation (R <sup>2</sup> )	Number of pairs	Average ratio of Y/X ± standard deviation		Distribution <sup>c</sup>				Average difference (Ȳ - X̄) ± Std. Dev. (μg/m <sup>3</sup> )		Unc. <sup>d</sup> Ȳ - X̄	T <sup>e</sup>	P <sup>f</sup>	AE (%) <sup>g</sup>	Begin date	End date
		Regression slope ± uncertainty	Intercept ± uncertainty			<1σ	1σ-2σ	2σ-3σ	>3σ	(Ȳ - X̄) ± Std. Dev. (μg/m <sup>3</sup> )									
AN300.2	AN300.1	0.95 ± 0.01	0.64 ± 0.31	0.98	151	0.99 ± 0.12						-0.38 ± 2.72	-1.74	0.0845	-1.0	01/06/99	01/26/02		
RP2K.2	RP2K.1	0.91 ± 0.02	0.34 ± 0.48	0.98	77	0.93 ± 0.13						-1.86 ± 3.14	-5.19	0.0000	-7.1	09/11/02	12/29/03		
AN300.1	AN100	0.98 ± 0.02	1.47 ± 0.50	0.98	106	1.10 ± 0.16		44	37	16	9	1.06 ± 3.66	2.97	0.0037	10.1	07/05/99	02/01/02		
AN300.2	AN100	0.92 ± 0.01	1.63 ± 0.28	0.99	148	1.04 ± 0.11		89	40	16	3	0.02 ± 3.01	2.50	0.10	0.9222	3.9	07/05/99	11/04/02	
RP2K.1	AN100	0.91 ± 0.01	1.11 ± 0.29	0.98	103	1.00 ± 0.14		69	28	3	3	-0.50 ± 2.45	2.50	-2.07	0.0407	0.1	02/07/02	12/29/03	
RP2K.2	AN100	0.87 ± 0.01	1.18 ± 0.31	0.99	66	0.96 ± 0.20		39	17	7	3	-1.59 ± 2.93	2.50	-4.40	0.0000	-3.8	09/11/02	12/29/03	
SFS	AN100	0.85 ± 0.02	1.02 ± 0.65	0.98	60	0.97 ± 0.31		18	16	12	14	-3.04 ± 6.27	2.76	-3.76	0.0004	-2.5	12/02/99	01/31/01	
AN400	AN100	0.96 ± 0.01	0.89 ± 0.19	0.99	239	1.03 ± 0.19		155	63	13	8	-0.07 ± 2.44	2.45	-0.46	0.6478	3.1	07/05/99	12/29/03	
DICHOT.1	AN100	0.81 ± 0.02	2.71 ± 0.87	0.91	114	0.97 ± 0.10		75	33	4	2	-1.75 ± 9.10	2.50	-2.05	0.0424	-3.1	07/05/99	10/28/01	
M1ST	AN100	0.98 ± 0.01	1.25 ± 0.31	0.98	185	1.11 ± 0.25		96	37	21	31	0.87 ± 3.19	2.50	3.72	0.0003	11.3	04/06/00	12/29/03	
BAM25	AN100	0.95 ± 0.01	4.40 ± 0.46	0.96	206	1.30 ± 0.33		42	36	26	102	3.34 ± 5.07	2.50	9.46	0.0000	29.5	12/20/99	09/24/03	
TEOM25	AN100	0.40 ± 0.03	4.66 ± 0.88	0.55	222	0.78 ± 0.37		55	47	15	105	-9.62 ± 18.95	2.50	-7.57	0.0000	-21.8	07/11/99	12/29/03	
DUSTTRAK	AN100	1.86 ± 0.07	12.46 ± 1.91	0.84	142	2.73 ± 0.98		1	2	1	138	29.34 ± 22.97	2.50	15.22	0.0000	173.4	04/30/00	06/20/03	
GREENTEK	AN100	1.44 ± 0.06	-2.95 ± 1.85	0.91	66	1.20 ± 0.39		13	7	10	36	7.72 ± 13.95	2.50	4.49	0.0000	19.8	10/04/01	01/21/03	
AN400	SFS	1.10 ± 0.02	0.57 ± 0.84	0.97	63	1.14 ± 0.20		19	17	10	17	2.97 ± 5.69	2.71	4.14	0.0001	13.7	12/02/99	01/31/01	
MOUDI	SFS	1.09 ± 0.21	6.28 ± 16.15	0.68	15	1.21 ± 0.39		5	1	1	8	12.54 ± 27.00	3.28	1.80	0.0935	21.3	12/15/00	02/03/01	
DUSTTRAK	BAM25	2.13 ± 0.03	3.41 ± 0.80	0.89	830	2.33 ± 0.79						30.34 ± 24.73	35.35	0.0000	133.4	04/26/00	06/23/03		
GREENTEK	BAM25	1.52 ± 0.03	-9.79 ± 0.97	0.89	373	1.04 ± 0.39						4.91 ± 14.94	6.35	0.0000	3.6	09/16/01	01/22/03		
BAM10	HTVOL10V	1.05 ± 0.03	4.76 ± 1.32	0.95	105	1.18 ± 0.23						7.02 ± 8.48	8.48	0.0000	18.2	12/08/99	08/29/01		
TEOM10	HTVOL10V	0.67 ± 0.05	2.17 ± 2.45	0.65	111	0.72 ± 0.23						-11.51 ± 17.66	-6.87	0.0000	-27.5	07/11/99	06/24/01		
RAD25	AN100	4.07 ± 0.13	-9.52 ± 4.97	0.90	115	3.34 ± 1.02										11/20/00	08/25/03		
RAD	AN100	4.49 ± 0.08	-9.79 ± 2.42	0.95	192	3.67 ± 1.18										03/25/00	08/01/03		
RAD	SFS	5.46 ± 0.17	7.08 ± 7.40	0.93	74	5.31 ± 1.90										03/25/00	02/03/01		

<sup>a</sup> See Table 2 for sampler descriptions.

<sup>b</sup> Ordinary least squares method does not weight variables by their precisions (Bevington and Robinson 1992).

<sup>c</sup> Number of sample concentration differences between stated precision intervals ( $s$ ) for the difference.

<sup>d</sup> Uncertainty of the average difference between Y and X.

<sup>e</sup> Paired-difference T-test.

<sup>f</sup> Significant probability:  $P < 0.05$  implies the difference between Y and X is significant.

<sup>g</sup> Average error. (i.e., difference between measurements):  $AE = 100 \frac{1}{N} \sum_{i=1}^N \frac{Y_i - X_i}{X_i}$ .

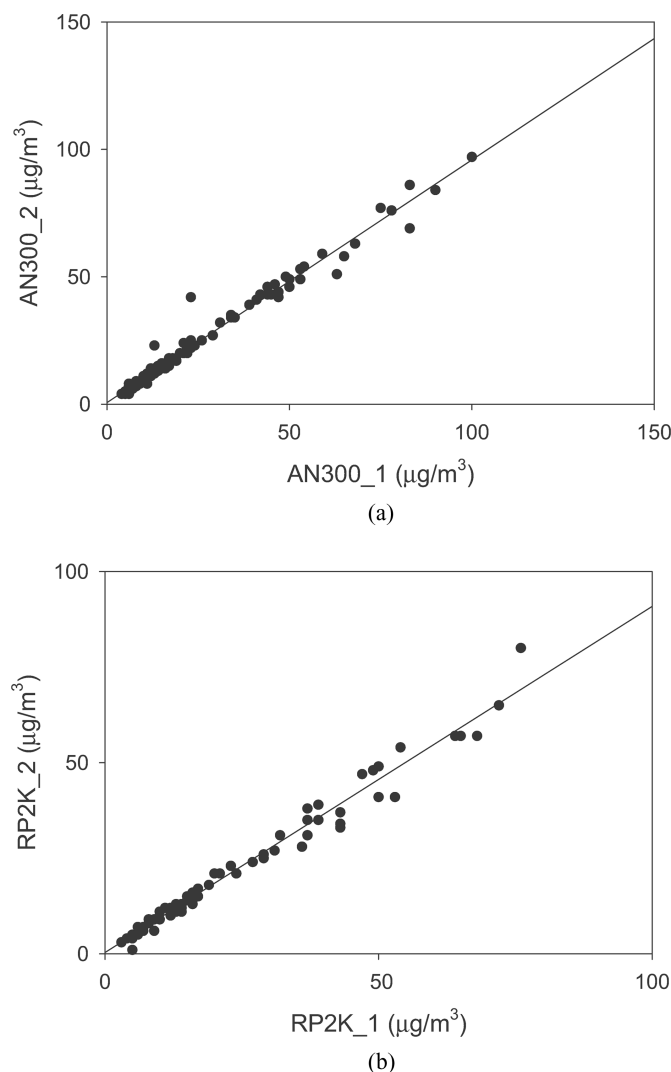


FIG. 2. Comparison of (a) two collocated Andersen RAAS 300 (AN300) and (b) two collocated R&P 2000 (RP2K) PM<sub>2.5</sub> FRM samplers at the Fresno Supersite, CA.

## RESULTS AND DISCUSSION

### Fresno Supersite

Table 3 compares results for the 20 samplers collocated at the Fresno Supersite (FSF). The start and end dates for several samplers extend beyond the CRPAQS period. The first six entries in Table 3 compare PM<sub>2.5</sub> FRM samplers. In each case, the  $R^2$  was 0.98 or 0.99. There were two Andersen RAAS 300 (AN300) and two R&P 2000 (RP2K) samplers at this site during different time periods. Figure 2 shows the collocated comparisons for each model. The average paired differences were  $-0.38$  and  $-1.86$  μg/m<sup>3</sup> (Table 3) for the AN300 and RP2K, respectively. While there may have been a larger paired difference (AE) for RP2K<sub>2</sub> compared to RP2K<sub>1</sub>, the AE was less than 10%.

The AN100 served as the benchmark (X) for most of the PM<sub>2.5</sub> comparisons in Table 3. The  $R^2$  for the comparison

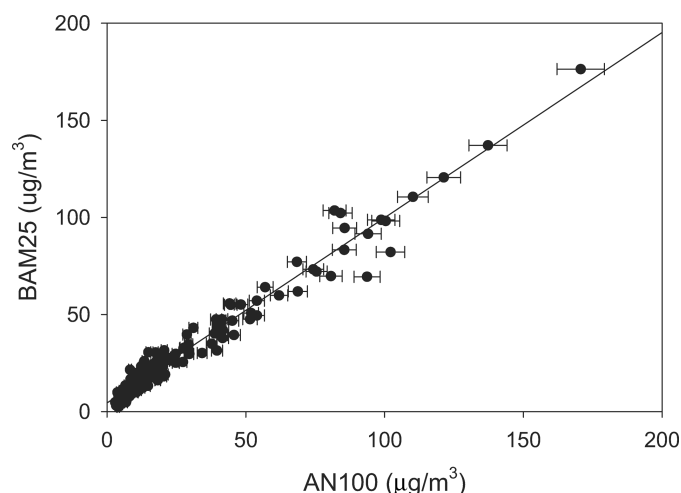


FIG. 3. Comparison of Andersen RAAS 100 (AN100) and Met One PM<sub>2.5</sub> BAM (BAM25) samplers at the Fresno Supersite, CA.

of this sampler with the two RP2K, two AN300, SFS, and Met One SASS (M1ST) samplers was 0.98 or 0.99. Except for the SFS, the respective differences ( $Y - X$ ), on average, were less than twice their measurement uncertainties for most data pairs. For most of these comparisons, the AE was less than 10%. The AE was not consistently higher for PM<sub>2.5</sub> FRM concentrations less than 25 μg/m<sup>3</sup>. Note that except for the SFS, the average differences ( $\overline{Y - X}$ ) between the AN100 and the other PM<sub>2.5</sub> filter samplers were less than the average difference between the two collocated RP2K FRM samplers.

Four continuous PM<sub>2.5</sub> mass monitors were operated at FSF: a Met One BAM, R&P TEOM, TSI DustTrak, and GreenTek photometer. Figure 3 compares the AN100 with 24-h averaged PM<sub>2.5</sub> (BAM25). While the slope of 0.95, intercept of 4.4 μg/m<sup>3</sup>,  $R^2$  of 0.96, and  $\overline{Y - X}$  of 3.3 μg/m<sup>3</sup> are reasonable, most of the disagreement occurs for PM<sub>2.5</sub> less than 25 μg/m<sup>3</sup>, for which the AE was 37% ( $N = 158$ ). For PM<sub>2.5</sub> above 25 μg/m<sup>3</sup>, the AE was only 4.1% ( $N = 48$ ).

Table 3 indicates poor agreement between the AN100 and the TEOM, DustTrak, and GreenTek. While the  $R^2$  was reasonable for the DustTrak ( $R^2 = 0.84$ ) and GreenTek ( $R^2 = 0.91$ ), this was not the case for the TEOM25 ( $R^2 = 0.55$ ). Since both DustTrak and GreenTek mass appear to be overestimated, the assumed scattering efficiencies in both cases must be too low. The TEOM25 values were lower ( $\overline{Y - X} = -9.62$  μg/m<sup>3</sup>) than AN100 FRM. The air-sampling stream in the TEOM was heated to 50°C to minimize temperature-related changes in the tapered element. This heating evaporates volatile compounds such as NH<sub>4</sub>NO<sub>3</sub>, which constitutes a large fraction of PM<sub>2.5</sub> mass in the SJV, especially in winter when colder temperatures shift the ammonia (NH<sub>3</sub>)-nitric acid (HNO<sub>3</sub>)-NH<sub>4</sub>NO<sub>3</sub> equilibrium to the particle phase (Chow et al. 1993, 2005). Some of the volatile organic compounds (VOCs) may also be removed by heating. Chung et al. (2001) and Charron et al. (2004) reported

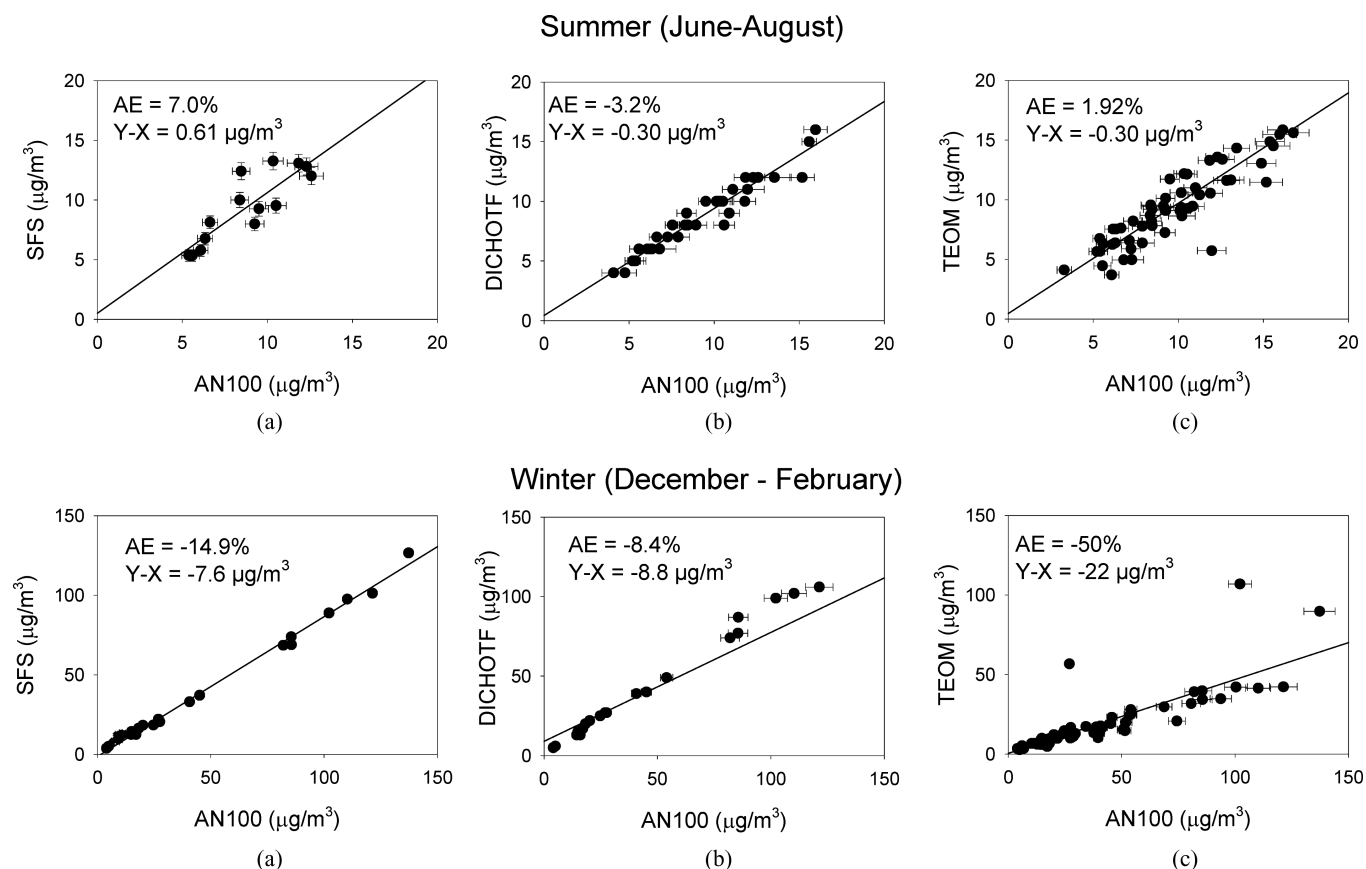


FIG. 4. Seasonal comparisons between Andersen PM<sub>2.5</sub> RAAS 100 (AN100) FRM sampler and collocated: (a) DRI sequential filter samplers (SFS); (b) Andersen PM<sub>2.5</sub> dichotomous (DICHOTF); and (c) PM<sub>2.5</sub> TEOM at the Fresno Supersite, CA (Summer = June–August; Winter = December–February).

similar comparisons of TEOM with AN300 and R&P 2025 (RP225) FRM samplers, respectively.

Table 3 also shows negative  $\bar{Y} - \bar{X}$  and AE for the SFS and dichotomous (DICHOTF) samplers, which might be explained by evaporative loss of  $\text{NH}_4\text{NO}_3$  in each sampler during the colder months. Figure 4 shows comparisons between the SFS, DICHOTF, and TEOM25 samplers and the AN100 for summer (June–August) and winter (December–February) samples. In each case,  $\bar{Y} - \bar{X}$  and AE are more negative during the winter season. Heating in the TEOM resulted in a negative difference ( $Y - X$ ) of about  $22 \mu\text{g}/\text{m}^3$  between summer and winter (Figure 4) (see Hering and Cass 1999). The corresponding seasonal differences in  $Y - X$  for the SFS and DICHOTF samplers were  $\sim 8 \mu\text{g}/\text{m}^3$  for both. The SFS was equipped with an anodized aluminum denuder that removes the gaseous  $\text{HNO}_3$  upstream of the filter. This shifts the equilibrium to the gas phase and enhances evaporation of  $\text{NH}_4\text{NO}_3$  from the Teflon-membrane filter on which mass is measured. While there was relatively more evaporation during summer, the impact on PM<sub>2.5</sub> was most severe during winter.  $\text{NH}_4\text{NO}_3$  evaporation may explain why the DICHOTF sampler concentrations were lower relative to the AN100 during winter than summer; although, it is not clear why the DICHOTF sampler

inlet would remove  $\text{HNO}_3$  more effectively than the AN100 inlet. The SFS sampler collects volatilized  $\text{NO}_3^-$  on sodium chloride-impregnated cellulose-fiber filters behind quartz-fiber filters. If the  $\text{NH}_4\text{NO}_3$  equivalent (i.e., 1.29 times volatilized  $\text{NO}_3^-$  from the backup filter) is added to the SFS mass measured on a Teflon-membrane filter, the average difference between SFS and AN100 changes from  $-3.04$  (Table 3) to  $-0.46 \mu\text{g}/\text{m}^3$ .

The Andersen GMW-1200 PM<sub>10</sub> FRM sampler (HIVOL10V) at FSF was compared with collocated BAM10 and TEOM10 samplers, both of which are designated as FEMs (Code of Federal Regulations 1988). Table 3 shows that the BAM10-HIVOL10V ( $R^2 = 0.95$ ) and TEOM10-HIVOL10V ( $R^2 = 0.65$ ) comparisons are similar to the corresponding PM<sub>2.5</sub> comparisons. The BAM10 read higher PM<sub>10</sub> than the HIVOL10V FRM; the AE was 21% for PM<sub>10</sub> FRM concentrations  $< 25 \mu\text{g}/\text{m}^3$  as compared to 11% for PM<sub>10</sub> FRM concentrations  $\geq 25 \mu\text{g}/\text{m}^3$ . Chang et al. (2001) attribute higher BAM measurements relative to integrated filter samplers to water absorption by hygroscopic species. The TEOM10 comparison is also analogous to the PM<sub>2.5</sub> case. While the overall AE was  $-28\%$ , it was higher in winter ( $-43\%$ ) than in summer (13.4%).

TABLE 4  
Sampler comparison at CRPAQS anchor sites

Site <sup>a</sup>	Sampler <sup>d</sup>		Ordinary least squares <sup>b</sup>		Correlation (R <sup>2</sup> )	Number of pairs	Average ratio of Y/X $\pm$ standard deviation	Distribution <sup>c</sup>			Average difference ( $\bar{Y} - \bar{X}$ ) $\pm$ Std. Dev.		Unc. <sup>d</sup> $\bar{Y} - \bar{X}$	T <sup>e</sup>	P <sup>f</sup>	AE(%) <sup>g</sup>	Begin date	End date
	Y	X	Regression slope $\pm$ uncertainty	Intercept $\pm$ uncertainty				<1 $\sigma$	1 $\sigma$ -2 $\sigma$	>3 $\sigma$								
BAC AN300-2	AN300-1	AN300-1	0.97 $\pm$ 0.01	0.30 $\pm$ 0.18	0.99	265	1.01 $\pm$ 0.41				-0.45 $\pm$ 2.09			-3.48	0.0006	1.33	01/07/99	06/26/03
BAC RP225-2	RP225-1	RP225-1	0.99 $\pm$ 0.03	-0.16 $\pm$ 0.55	0.99	13	0.98 $\pm$ 0.04				-0.34 $\pm$ 0.79			-1.56	0.1450	-2.12	07/14/03	12/23/03
BAC MIST-2	MIST	MIST	0.95 $\pm$ 0.02	0.76 $\pm$ 0.56	0.88	272	1.01 $\pm$ 0.40				-0.21 $\pm$ 5.66			-0.62	0.5349	0.93	05/25/01	12/29/03
BAC MIST	AN300-1	AN300-1	1.03 $\pm$ 0.01	1.12 $\pm$ 0.38	0.96	215	1.16 $\pm$ 0.57				1.76 $\pm$ 3.53			7.33	0.0000	15.64	05/25/01	06/26/03
BAC SFS	AN300-1	AN300-1	0.82 $\pm$ 0.03	3.73 $\pm$ 1.42	0.91	66	1.13 $\pm$ 0.95	12	22	9	-1.87 $\pm$ 9.79	3.76		-1.55	0.1249	12.75	12/08/99	02/03/01
BAC DICHOTF-1	AN300-1	AN300-1	0.87 $\pm$ 0.01	0.15 $\pm$ 0.33	0.97	197	0.87 $\pm$ 0.09				-2.99 $\pm$ 4.31			-9.74	0.0000	-13.33	01/03/99	12/29/00
BAC BAM25	AN300-1	AN300-1	0.97 $\pm$ 0.01	-2.25 $\pm$ 0.26	0.98	333	0.79 $\pm$ 0.25				-2.94 $\pm$ 3.39			-15.80	0.0000	-21.23	01/22/00	02/05/01
BAC BAM10	HIVOL10V	HIVOL10V	1.08 $\pm$ 0.02	8.05 $\pm$ 1.14	0.96	120	1.29 $\pm$ 0.15				11.85 $\pm$ 6.94			18.70	0.0000	28.60	01/22/00	02/03/01
BAC TEOM10	HIVOL10V	HIVOL10V	0.66 $\pm$ 0.03	12.55 $\pm$ 1.79	0.69	179	0.96 $\pm$ 0.20				-3.70 $\pm$ 14.06			-3.52	0.0006	-4.19	07/02/99	06/30/01
BAC RAD	AN300-1	AN300-1	5.63 $\pm$ 0.08	-24.71 $\pm$ 2.64	0.94	335	3.88 $\pm$ 1.28										01/08/00	02/09/01
BAC RAD	SFS	SFS	6.09 $\pm$ 0.23	-25.79 $\pm$ 11.31	0.91	70	4.80 $\pm$ 2.34										01/07/2000	02/03/2001
BTI MINIVOL25	SFS	SFS	1.04 $\pm$ 0.06	-3.81 $\pm$ 2.37	0.98	9	0.82 $\pm$ 0.35	2	5	2	-2.50 $\pm$ 3.88	2.70		-1.94	0.0890	-17.53	12/02/00	01/31/01
BTI BAM25	SFS	SFS	1.06 $\pm$ 0.04	1.78 $\pm$ 1.36	0.97	21	1.21 $\pm$ 0.35	14	2	2	3.29 $\pm$ 3.45	3.65		4.36	0.0003	21.06	12/02/00	02/03/01
BTI RAD	SFS	SFS	5.99 $\pm$ 0.31	-4.06 $\pm$ 10.02	0.95	22	5.94 $\pm$ 1.57										12/08/00	02/03/01
SNFH MINIVOL25	SFS	SFS	1.01 $\pm$ 0.06	-2.54 $\pm$ 1.32	0.97	11	0.81 $\pm$ 0.35	2	7	2	-2.43 $\pm$ 2.40	2.68		-3.35	0.0073	-18.53	12/02/00	01/31/01
SNFH BAM25	SFS	SFS	1.19 $\pm$ 0.05	-2.19 $\pm$ 1.09	0.97	23	1.07 $\pm$ 0.18	14	5	3	1.64 $\pm$ 3.45	3.22		2.29	0.0321	7.21	12/02/00	02/03/01
SNFH RAD	SFS	SFS	5.91 $\pm$ 0.45	-10.99 $\pm$ 10.15	0.89	24	5.21 $\pm$ 1.18										12/02/00	02/03/01
ANGI BAM25	SFS	SFS	0.67 $\pm$ 0.06	3.26 $\pm$ 2.39	0.69	65	0.87 $\pm$ 0.39	19	13	5	-6.40 $\pm$ 16.64	3.43		-3.10	0.0029	-9.61	01/25/00	02/03/01
ANGI MOUDI	SFS	SFS	0.85 $\pm$ 0.08	6.60 $\pm$ 5.13	0.90	15	1.06 $\pm$ 0.29	6	4	2	-1.80 $\pm$ 11.98	3.18		-0.58	0.5704	5.64	12/15/00	02/03/01
ANGI RAD	SFS	SFS	4.91 $\pm$ 0.43	9.73 $\pm$ 18.29	0.68	64	5.15 $\pm$ 2.50										02/06/00	02/03/01

<sup>a</sup>See Table 1 for site names and Table 2 for sampler descriptions.

<sup>b</sup>Ordinary Least Squares method does not weight variables by their precisions (Bevington and Robinson 1992).

<sup>c</sup>Number of sample concentration differences between stated precision intervals (s) for the difference.

<sup>d</sup>Uncertainty of the average difference between Y and X.

<sup>e</sup>Paired-difference T-test.

<sup>f</sup>Significant probability:  $P < 0.05$  implies the difference between Y and X is significant.

<sup>g</sup>Average error:  $AE = 100 \frac{1}{N} \sum_{i=1}^N \frac{Y_i - X_i}{X_i}$ .



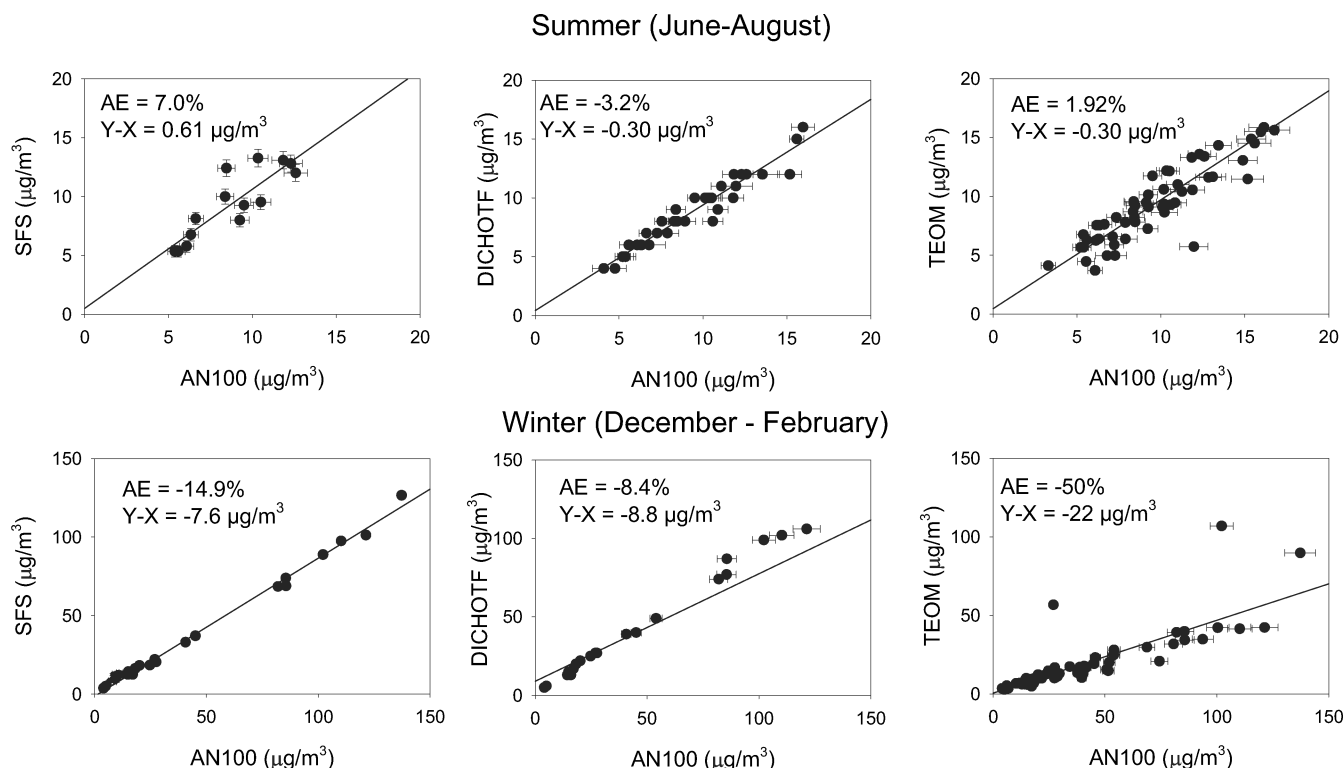


FIG. 5. Comparison of two collocated  $PM_{2.5}$  (a) Andersen RAAS 300 (AN300) FRM; (b) R&P 2025 (RP225) FRM; and (c) Met One Speciation (M1ST) samplers at Bakersfield, CA.

Fresno was the only CRPAQS site with a Radiance Research M903 nephelometer preceded by a  $PM_{2.5}$  size-selective inlet (RAD25). A Radiance Research nephelometer (RAD) for measuring TSP  $B_{sp}$  (i.e., total  $B_{sp}$ ) was also located there. Table 3 gives comparison statistics for  $PM_{2.5}$  measured with the AN100 and SFS samplers and the RAD25 and RAD nephelometers. The slope of the regression and the average ratio of  $Y/X$  are two estimates of the mass scattering efficiency ( $m^2/g$ ). While particles larger than  $2.5 \mu m$  contribute to total  $B_{sp}$  (RAD), the signal was dominated by fine particles because they scatter light more efficiently than larger ones. For example, average RAD25 and RAD at FSF were 89 and  $95 Mm^{-1}$ , respectively. Based on the slopes, the average mass scattering efficiencies for RAD25 and RAD were 4.1 and  $4.5 m^2/g$ , respectively. Based on the average ratios of  $Y/X$ , the corresponding average mass scattering efficiencies for RAD25 and RAD were 3.3 and  $3.7 m^2/g$ , respectively.

#### CRPAQS Anchor Sites

Comparison statistics for the remaining CRPAQS anchor sites are presented in Table 4. Paired  $PM_{2.5}$  AN300 FRM, RP225 FRM, and M1ST samplers were used at BAC over different time periods. Comparisons for collocated samples taken at the same time are shown in Figure 5. The AN300 pairs and RP225 pairs agreed closely with slopes  $\geq 0.97$ , intercepts  $< 1 \mu g/m^3$ ,  $R^2 = 0.99$ ,  $Y/X$  between 0.98 and 1.01,  $|\bar{Y} - \bar{X}| < 0.5 \mu g/m^3$ , and  $|AE| \sim 2\%$ . However, according to the paired difference

T-test, the two AN300 samplers were significantly different, while the two RP225 samplers were not. This is due to the small sample size ( $N = 13$ ) for the RP225 comparison. The smaller the number of observations, the more difficult it is to detect differences in parametric statistical tests. The M1ST comparison was influenced by three obvious outliers (Figure 5). Removing these samples increased the slope and  $R^2$  to 0.97 and 0.99, respectively, and decreased the intercept to  $0.16 \mu g/m^3$ .

As at FSF,  $PM_{2.5}$  DICHOTF sampler concentrations were consistently lower than the corresponding AN300. The comparison between the AN300 and SFS sampler also showed a slope less than 1 and a  $\bar{Y} - \bar{X}$  of  $-1.87 \mu g/m^3$ . However, in this case, the average ratio ( $\bar{Y}/\bar{X}$ ) was larger than 1 (1.13) with positive AE (12.8%). Figure 6, which displays the SFS versus AN300 comparison, shows five consecutive samples from 4/12/00 to 5/6/00 where the SFS concentrations were all higher than those of the AN300. The corresponding BAM25 concentrations agreed much more closely with the AN300. Higher-than-expected SFS concentrations suggest a sample volume error that may have been related to power interruptions. If these five data points are excluded, the slope (0.86), intercept ( $0.94 \mu g/m^3$ ),  $R^2$  (0.98), average ratio ( $\bar{Y}/\bar{X} = 0.93$ ),  $\bar{Y} - \bar{X}$  ( $-3.74 \mu g/m^3$ ), and AE ( $-6.8\%$ ) are more in line with the corresponding comparison of the SFS versus AN100 at FSF (Table 3). It is worth noting that the five SFS outliers are also found in a comparison between SFS and RAD.

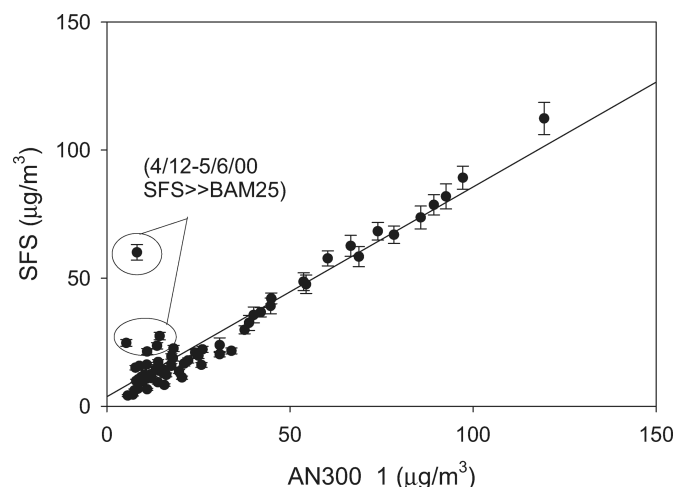


FIG. 6. Comparison of Andersen PM<sub>2.5</sub> RAAS 300 (AN300) and DRI sequential filter samplers (SFS) at Bakersfield, CA.

Based on the average difference ( $\bar{Y} - \bar{X}$ ), the BAM25 was lower than the AN300 FRM at BAC, but higher than the AN100 FRM at FSF (Table 3). The FSF time series was considerably longer and there could be differences in the BAM calibrations between the two sites. BAM10 concentrations were higher than the PM<sub>10</sub> FRM (HIVOL10V) concentrations at BAC, as was the case at FSF, evidenced by large positive regression intercepts ( $8.1 \mu\text{g}/\text{m}^3$ ) and  $\bar{Y} - \bar{X}$  ( $11.9 \mu\text{g}/\text{m}^3$ ). These results are also consistent with those reported by Chang et al. (2001). The TEOM10 yielded lower concentrations than the HIVOL10V, although  $\bar{Y} - \bar{X}$  was smaller ( $-3.7 \mu\text{g}/\text{m}^3$ ) at BAC than it was at FSF ( $-11.5 \mu\text{g}/\text{m}^3$ , Table 3). The mass scattering efficiencies (RAD versus AN300 and SFS) at BAC were 10–23% higher than those at FSF.

Since the number of samplers was limited at the BTI, SNFH, and ANGI CRPAQS anchor sites, the SFS sampler was used as the reference (X). The MINIVOL25 samplers measured lower PM<sub>2.5</sub> than the SFS at BTI and SNFH, although the average difference was within measurement uncertainty at both sites. The  $R^2$  was 0.98 at BTI and 0.97 at SNFH. The comparison between the SFS and MOUDI and SFS at ANGI was better than at FSF. The  $\bar{Y} - \bar{X}$  and  $R^2$  were  $-1.8 \mu\text{g}/\text{m}^3$  and 0.90, respectively, at ANGI, and  $12.5 \mu\text{g}/\text{m}^3$  and 0.68, respectively, at FSF.

Table 5 summarizes comparisons between RAD and SFS as mass scattering efficiencies estimated from the slope of Y on X and the average ratio of Y/X. The mass scattering efficiencies at the five sites were similar. For all sites, the average slope ( $5.7 \pm 0.5 \text{ m}^2/\text{g}$ ) was similar to the average ratio of Y/X ( $5.3 \pm 0.4 \text{ m}^2/\text{g}$ ).

### CRPAQS Satellite Sites

PM<sub>2.5</sub> FRM (AN300) samplers were located at all satellite sites, except Modesto (M14), and PM<sub>10</sub> FRM (HIVOL10V) samplers were at all sites, except for Visalia (VCS). Pair-wise

TABLE 5

Relationship between PM<sub>2.5</sub> DRI sequential filter sampler (SFS) mass and Radiance Research open-air nephelometer (RAD) light scattering ( $B_{sp}$ ) at the five CRPAQS anchor sites

Site	Mass scattering efficiency ( $\text{m}^2/\text{g}$ )	
	Slope <sup>a</sup>	$B_{sp}/\text{PM}_{2.5}$
Bethel Island (BTI)	6.0	5.9
Sierra Nevada Foothills (SNFH)	5.9	5.2
Fresno (FSF)	5.5	5.3
Bakersfield (BAC)	6.1	4.8
Angiola (ANG1)	4.9	5.2
Averages $\pm$ Std. Dev.	$5.7 \pm 0.5$	$5.3 \pm 0.4$

<sup>a</sup>Slope of  $B_{sp}$  on PM<sub>2.5</sub> (Table 4).

comparisons are shown in Table 6. At COP,  $R^2$  was  $\geq 0.97$  for the DICHOTF, MINIVOL25, and MINIVOL10 comparisons. The  $\bar{Y} - \bar{X}$  was less than its uncertainty for both PM<sub>2.5</sub> and PM<sub>10</sub> MiniVols. The AEs were larger than 10%, except for the MINIVOL10. At LVR1,  $R^2$  was  $\geq 0.96$ , including the TEOM10 versus HIVOL10V comparison. Similar comparability was found at SJ4 ( $R^2 = 0.96$ ). TEOM comparisons at FSF (Table 3) and BAC (Table 4) were more variable.

The TEOM10 values were lower than filter measurements at LVR1 and SJ4, as well as at M14 and S13, where the  $R^2$  was much lower, 0.73 and 0.78, respectively. The DICHOTF agreed well with the AN300 at SJ4 and SOH, with  $R^2$  equal to 0.99 in both cases, and  $\bar{Y}/\bar{X}$  equal to 0.92 and 0.97, respectively. At VCS, the DICHOTF measured concentrations lower than the AN300 ( $\bar{Y}/\bar{X} = 0.83$ ), although the  $R^2$  was 0.99. The difference between the MINIVOL25 and AN300 ( $\bar{Y} - \bar{X}$ ) was less than twice its uncertainty in the majority of cases at all sites.

The PM<sub>2.5</sub> AN300 FRM and RAD samplers were deployed at five of the seven CRPAQS satellite sites. Mass scattering efficiencies estimated from the slopes of Y on X and the average ratios of Y/X at the satellite sites are presented in Table 7. The average and standard deviation of the slope and ratio are  $4.6 \pm 0.8$  and  $4.4 \pm 0.8 \text{ m}^2/\text{g}$ , respectively. These efficiencies are consistently lower than those of  $5.7 \pm 0.5$  and  $5.3 \pm 0.4 \text{ m}^2/\text{g}$ , respectively, derived from the SFS sampler (Table 5). This difference arises because the PM<sub>2.5</sub> mass measured with the SFS was consistently 2 to  $3 \mu\text{g}/\text{m}^3$  lower than that measured by the Andersen FRM samplers (Tables 3 and 4).

### Comparison Summary

To generalize the comparability measures from different samplers and locations, the results in Tables 3, 4, and 6 are reorganized to reflect only those comparisons where the X sampler was either a PM<sub>2.5</sub> FRM (AN100 or AN300) or a PM<sub>10</sub> FRM (HIVOL10V). The results, sorted and averaged by the Y sampler (AN300, BAM10, BAM25, DICHOTF, M1ST, MINIVOL25,

TABLE 6  
Sampler comparison at CRPAQS satellite sites

Site <sup>a</sup>	Sampler <sup>a</sup>		Ordinary least squares <sup>b</sup> (μg/m <sup>3</sup> )		Correlation (R <sup>2</sup> )	Number of pairs	Average ratio of Y/X				Distribution <sup>c</sup>			Average difference ( $\bar{Y} - \bar{X}$ ) ± Std. Dev. (μg/m <sup>3</sup> )		Unc. <sup>d</sup> $\bar{Y} - \bar{X}$	T <sup>e</sup>	P <sup>f</sup>	AE(%) <sup>g</sup>	Begin date	End date
	Regression slope ± uncertainty		Intercept ± uncertainty	± standard deviation			1σ	1σ-2σ	2σ-3σ	3σ	Std. Dev.	±									
	Y	X																			
COP	DICHOTF.1	AN300.1	0.88 ± 0.02	-0.73 ± 0.35	0.98	35	0.82 ± 0.06							-2.50 ± 1.50			-9.86	0.0000	-17.56	01/06/99	03/31/00
COP	MINIVOL25	AN300.1	1.05 ± 0.02	-3.62 ± 0.88	0.97	51	0.81 ± 0.25	20	21	7	3			-2.32 ± 4.86		3.63	-3.41	0.0013	-18.61	03/01/00	02/03/01
COP	BAM25	AN300.1	0.92 ± 0.07	3.08 ± 1.84	0.92	15	1.19 ± 0.51							1.44 ± 4.15			1.34	0.2008	19.10	09/15/00	11/14/00
COP	MINIVOL10	HIVOL10V	0.98 ± 0.07	-1.97 ± 4.27	0.98	6	0.90 ± 0.14	3	1	2	0			-3.06 ± 4.63		4.45	-1.62	0.1662	-9.56	10/09/00	11/14/00
COP	BAM10	HIVOL10V	1.25 ± 0.12	3.25 ± 6.93	0.93	10	1.31 ± 0.19							16.39 ± 10.36			5.01	0.0007	31.32	09/15/00	11/14/00
COP	RAD	AN300.1	5.09 ± 0.31	23.05 ± 16.21	0.91	27	5.65 ± 1.13													10/09/00	02/03/01
LVR1	MINIVOL25	AN300.1	0.86 ± 0.02	-1.23 ± 0.46	0.96	67	0.71 ± 0.28	20	33	8	6			-3.28 ± 3.66		2.61	-7.35	0.0000	-29.14	12/02/99	02/03/01
LVR1	TEOM10	HIVOL10V	0.74 ± 0.04	2.53 ± 0.86	0.97	16	0.88 ± 0.11							-2.68 ± 4.25			-2.52	0.0234	-11.63	01/07/00	03/31/00
LVR1	RAD	AN300.1	4.09 ± 0.10	1.06 ± 3.50	0.98	31	4.08 ± 0.63													11/20/00	02/21/01
MM14	TEOM10	HIVOL10V	0.65 ± 0.04	5.57 ± 1.69	0.73	118	0.83 ± 0.18							-7.40 ± 13.86			-5.80	0.0000	-16.99	07/05/99	06/30/01
S13	DICHOTF.1	AN300.1	0.89 ± 0.03	2.16 ± 0.63	0.90	103	1.10 ± 0.24							0.46 ± 4.74			0.98	0.3311	10.10	12/13/98	12/14/00
S13	MINIVOL25	AN300.1	0.93 ± 0.03	-2.12 ± 0.85	0.93	65	0.71 ± 0.30	20	23	15	7			-3.36 ± 4.88		2.68	-5.54	0.0000	-28.65	12/02/99	02/03/01
S13	TEOM10	HIVOL10V	0.70 ± 0.03	2.48 ± 1.12	0.78	131	0.81 ± 0.18							-6.01 ± 8.89			-7.74	0.0000	-19.46	07/05/99	06/30/01
S14	M1ST	AN300.1	0.90 ± 0.03	3.65 ± 0.54	0.85	153	1.26 ± 0.39							2.18 ± 4.36			6.17	0.0000	26.46	02/10/00	04/26/02
S14	DICHOTF.1	AN300.1	0.88 ± 0.01	0.24 ± 0.23	0.99	48	0.92 ± 0.27							-1.50 ± 1.83			-5.69	0.0000	-7.89	03/01/99	02/24/00
S14	BAM25	AN300.1	0.94 ± 0.03	2.63 ± 0.78	0.91	127	1.17 ± 0.73							1.15 ± 5.60			2.31	0.0224	16.57	05/24/00	02/15/01
S14	TEOM10	HIVOL10V	0.82 ± 0.02	1.46 ± 0.77	0.96	56	0.88 ± 0.11							-3.59 ± 4.14			-6.49	0.0000	-11.56	07/05/99	05/30/00
S14	RAD	AN300.1	3.42 ± 0.08	0.00 ± 2.09	0.91	180	3.47 ± 1.95													02/09/01	
SOH	DICHOTF.1	AN300.1	0.95 ± 0.01	0.20 ± 0.19	0.99	106	0.97 ± 0.09							-0.65 ± 1.64			-4.09	0.0001	-2.87	01/12/99	12/26/00
SOH	MINIVOL25	AN300.1	1.01 ± 0.04	-3.04 ± 1.06	0.91	65	0.76 ± 0.36	19	31	9	6			-2.86 ± 6.14		2.99	-3.75	0.0004	-24.02	12/02/99	02/03/01
SOH	TEOM10	HIVOL10V	0.61 ± 0.04	6.67 ± 1.59	0.74	113	0.83 ± 0.18							-8.02 ± 13.46			-6.33	0.0000	-17.02	07/05/99	06/30/01
SOH	RAD	AN300.1	5.18 ± 0.29	-19.13 ± 9.85	0.92	31	4.30 ± 1.02													12/01/00	02/06/01
VCS	M1ST	AN300.1	0.97 ± 0.02	1.64 ± 0.46	0.96	110	1.08 ± 0.16							1.13 ± 2.80			4.22	0.0001	7.58	01/14/02	12/29/03
VCS	DICHOTF.1	AN300.1	0.79 ± 0.01	0.69 ± 0.36	0.99	61	0.83 ± 0.13							-4.90 ± 5.53			-6.92	0.0000	-17.02	01/18/99	03/01/00
VCS	MINIVOL25	AN300.1	0.94 ± 0.02	-2.66 ± 0.74	0.98	65	0.80 ± 0.21	16	25	19	5			-4.30 ± 4.40		3.90	-7.89	0.0000	-20.21	12/02/99	01/31/01
VCS	RAD	AN300.1	5.00 ± 0.40	-14.60 ± 28.13	0.91	18	4.69 ± 0.82													12/05/00	02/03/01

<sup>a</sup>See Table 1 for site names and Table 2 for sampler descriptions.

<sup>b</sup>Ordinary least squares method does not weight variables by their precisions (Bevington and Robinson, 1992).

<sup>c</sup>Number of sample concentration differences between stated precision intervals ( $\delta$ ) for the difference.

<sup>d</sup>Uncertainty of the average difference between Y and X.

<sup>e</sup>Paired-difference T-test.

<sup>f</sup>Significant probability:  $P < 0.05$  implies the difference between Y and X is significant.

<sup>g</sup>Average error:  $AE = 100 \frac{1}{N} \sum_{i=1}^N \frac{Y_i - X_i}{X_i}$ .

TABLE 7

Relationship between Andersen RAAS 300 (AN300) PM<sub>2.5</sub> FRM sampler mass and Radiance Research open nephelometer light scattering ( $B_{sp}$ ) at five CRPAQS satellite sites

Site	Mass scattering efficiency (m <sup>2</sup> /g)	
	Slope <sup>a</sup> (Y/X)	$B_{sp}/PM_{2.5}$ (Avg. ratio of Y/X)
Corcoran (COP)	5.1	5.6
Livermore (LVR1)	4.1	4.1
San Jose (SJ4)	3.4	3.5
Stockton (SOH)	5.2	4.3
Visalia (VCS)	5.0	4.7
Average $\pm$ Std. Dev.	4.6 $\pm$ 0.8	4.4 $\pm$ 0.8

<sup>a</sup> Slope of  $B_{sp}$  on PM<sub>2.5</sub> (Table 6).

SFS, and TEOM10), are presented in Table 8. The statistics are limited to the regression slope, intercept,  $R^2$ ,  $\bar{Y}/\bar{X}$ ,  $\bar{Y} - \bar{X}$ , and AE. Also presented is the distribution of  $|AE|$  (absolute difference) as the percentages of paired observations exhibiting an  $|AE|$  less than 10%, 10–20%, 20–30%, and greater than 30%.

Although least squares regression statistics are widely used to describe sampler comparisons, they might not be reliable, because: (1) they don't generally account for errors in the Y and X variables, and (2) they don't meet the statistical requirements for a normal distribution and uncorrelated random errors (Watson et al. 1984). Unless there is a true calibration offset, it is difficult to see why there should be significant intercepts in these comparisons. On the other hand, a high  $R^2$  implies that while two samplers may not be equivalent, the relationship may be functionally predictive (i.e., one sampler's measurement can be estimated from the other, or used as a surrogate for the other).

Table 8 demonstrates a general consistency in the comparison statistics. The best comparison was between the Andersen PM<sub>2.5</sub> FRM samplers, with an average slope of 0.96, intercept of 1.01  $\mu\text{g}/\text{m}^3$ ,  $R^2$  of 0.99,  $\bar{Y}/\bar{X}$  of 1.04,  $\bar{Y} - \bar{X}$  of 0.06  $\mu\text{g}/\text{m}^3$ , and AE of 3.6%. The absolute difference  $|AE|$  was less than 10% in 70% of the paired comparisons. The DICHOTF concentration was lower ( $-2 \mu\text{g}/\text{m}^3$ ) with respect to the FRM, as reported by Motallebi et al. (2003), but the AE was  $-7.4\%$ . However, the corresponding  $|AE|$  was less than 20% in 75% of the comparisons. The SFS was the only non-FRM sampler with  $\bar{Y}/\bar{X} = 0.95$ ,  $\bar{Y} - \bar{X} = -3.4 \mu\text{g}/\text{m}^3$ , and an  $|AE|$  of less than 5%. However, the  $|AE|$  was  $<10\%$  for 37% of the comparisons and 10–20% for 30% of the comparisons. The MINIVOL25 concentration was lower than the benchmark, with  $\bar{Y}/\bar{X} = 0.76$  and AE =  $-24\%$ . The average difference of  $-3.2 \mu\text{g}/\text{m}^3$  was comparable to its uncertainty of 3.1  $\mu\text{g}/\text{m}^3$  (estimated from the reported MINIVOL25 uncertainties, as described in the *Methods* section). However,  $|AE|$  was greater than 20% for 70% of the comparisons. The M1ST concentration was larger than the

benchmark ( $\bar{Y} - \bar{X} = 1.5 \mu\text{g}/\text{m}^3$ , AE = 15.2%). The  $|AE|$  was less than 20% for 70% of the comparisons.

The BAM25 results are consistently higher than the benchmark, except for samples acquired at BAC where values were lower. There were no obvious outliers in the BAC data, and the  $R^2$  was 0.98. The percentages of samples with a ratio (Y/X) greater than one were 76, 16, 67, and 54 at FSF, BAC, COP, and SJ4, respectively. This suggests a calibration difference in the BAC BAM25 with respect to those at the other sites. Excluding five outliers at BAC (Figure 6), the  $R^2$  for the SFS versus FRM comparison was 0.98. The average difference was  $-3.4 \mu\text{g}/\text{m}^3$  and the average AE was only  $-4.6\%$ . While there were clearly systematic differences in the BAM25 versus FRM comparisons, the two measures were highly correlated. The BAM25 is thus an effective surrogate for FRM mass where the goal is to examine temporal diurnal variability in PM<sub>2.5</sub> mass. In addition, a BAM25 collocated with an FRM sampler provides a means of identifying outliers.

The poorest comparison was for the BAM10, which displayed values much higher than the benchmark ( $\bar{Y}/\bar{X} = 1.26$ ,  $\bar{Y} - \bar{X} = 11.8 \mu\text{g}/\text{m}^3$ , AE = 26%), consistent with the observations of Chang et al. (2001). The TEOM10 showed a large average negative difference ( $-6.1 \mu\text{g}/\text{m}^3$ ), the largest deviation from a unity slope (0.69), and a high negative AE ( $-15.5\%$ ).

Sampling artifacts associated with organic carbon may influence sampler comparisons (McDow and Huntzicker 1990; Watson and Chow 2002; El-Zanan et al. 2005; Chow et al. 2006). A positive artifact results from the absorption of VOCs by quartz-fiber filters. This could influence the BAM25, BAM10, and HILVOL10 samplers, which employ quartz-fiber filters. A negative artifact may result from volatilization of VOCs from particles on Teflon or Teflon-coated filters. This could affect the FRM, DICHOTF, M1ST, MINIVOL, and SFS samplers. It is not possible to draw firm conclusions about the effect of organic carbon sampling artifacts on these comparisons.

### Measurement Uncertainties

Tables 3, 4, and 6 show that average differences ( $\bar{Y} - \bar{X}$ ) between filter samplers were on the order of their measurement uncertainties (when these were available). The average measurement uncertainties for the Fresno FRM and CRPAQS SFS samplers were 6.3 and 7.5%, respectively. For MINIVOL25 samplers, the average measurement uncertainties were 8.2% for PM<sub>2.5</sub>  $> 10 \mu\text{g}/\text{m}^3$ , 23% for PM<sub>2.5</sub> between 5 and 10  $\mu\text{g}/\text{m}^3$ , and 54% for PM<sub>2.5</sub> between 1 and 5  $\mu\text{g}/\text{m}^3$ .

Table 8 shows that the average difference between SFS and FRM samplers ( $-4.65\%$ ) was smaller than measurement uncertainties. Based on the uncertainties, a concentration gradient between FRM and SFS samplers of at least 15% should be seen. While this is also true for MINIVOL25 samplers for concentrations  $> 10 \mu\text{g}/\text{m}^3$ , it would be less accurate for lower concentrations, which would not be of great interest in the SJV. On the other hand, the difference between attainment and exceedance

TABLE 8  
Summary of PM<sub>2.5</sub> and PM<sub>10</sub> mass comparison

Site <sup>a</sup>	Sampler <sup>a</sup>		Regression		Correlation (R <sup>2</sup> ) <sup>b</sup>	Average ratio of Y/X	Average difference (Y - X)	AE(%) <sup>c</sup>	Distribution of  AE  Percent of samples <sup>b</sup>				Number of pairs
	Y	X	slope	Intercept					<10%	10–20%	20–30%	>30%	
FSF	AN300_1	AN100	0.98	1.47	0.98	1.10	1.06	10.13	48	35	12	5	106
FSF	AN300_2	AN300_1	0.95	0.64	0.98	0.99	-0.38	-0.99	81	14	2	3	151
FSF	AN300_2	AN100	0.92	1.63	0.99	1.04	0.02	3.93	64	27	8	1	148
BAC	AN300_2	AN300_1	0.97	0.30	0.99	1.01	-0.45	1.33	85	11	3	2	265
	Average		0.96	1.01	0.99	1.04	0.06	3.60	70	22	6	3	
FSF	BAM10	HIVOL10V	1.05	4.76	0.95	1.18	7.02	18.18	33	23	29	15	105
BAC	BAM10	HIVOL10V	1.08	8.05	0.96	1.29	11.85	28.60	11	22	38	30	120
COP	BAM10	HIVOL10V	1.25	3.25	0.93	1.31	16.39	31.32	0	40	30	30	10
	Average		1.13	5.35	0.95	1.26	11.75	26.03	15	28	32	25	
FSF	BAM25	AN100	0.95	4.40	0.96	1.30	3.34	29.52	25	19	16	40	206
BAC	BAM25	AN300_1	0.97	-2.25	0.98	0.79	-2.94	-21.23	29	24	15	32	333
COP	BAM25	AN300_1	0.92	3.08	0.92	1.19	1.44	19.10	40	20	27	13	15
SJ4	BAM25	AN300_1	0.94	2.63	0.91	1.17	1.15	16.57	43	21	9	28	127
	Average		0.95	1.97	0.94	1.11	0.75	10.99	34	21	17	28	
FSF	DICHOTF_1	AN100	0.81	2.71	0.91	0.97	-1.75	-3.13	70	25	4	1	114
BAC	DICHOTF_1	AN300_1	0.87	0.15	0.97	0.87	-2.99	-13.33	39	37	17	7	197
COP	DICHOTF_1	AN300_1	0.88	-0.73	0.98	0.82	-2.50	-17.56	9	54	26	11	35
S13	DICHOTF_1	AN300_1	0.89	2.16	0.90	1.10	0.46	10.10	48	34	11	8	103
SJ4	DICHOTF_1	AN300_1	0.88	0.24	0.99	0.92	-1.50	-7.89	38	46	10	6	48
SOH	DICHOTF_1	AN300_1	0.95	0.20	0.99	0.97	-0.65	-2.87	73	24	3	1	106
VCS	DICHOTF_1	AN300_1	0.79	0.69	0.99	0.83	-4.90	-17.02	5	26	61	8	61
	Average		0.87	0.77	0.96	0.93	-1.98	-7.39	40	35	19	6	
FSF	M1ST	AN100	0.98	1.25	0.98	1.11	0.87	11.31	57	17	17	9	185
BAC	M1ST	AN300_1	1.03	1.12	0.96	1.16	1.76	15.64	56	24	13	8	215
SJ4	M1ST	AN300_1	0.90	3.65	0.85	1.26	2.18	26.46	39	20	14	27	153
VCS	M1ST	AN300_1	0.97	1.64	0.96	1.08	1.13	7.58	52	29	14	5	110
	Average		0.97	1.91	0.94	1.15	1.48	15.25	51	23	15	12	
COP	MINIVOL25	AN300_1	1.05	-3.62	0.97	0.81	-2.32	-18.61	20	24	24	33	51
LVR1	MINIVOL25	AN300_1	0.86	-1.23	0.96	0.71	-3.28	-29.14	10	12	21	57	67
S13	MINIVOL25	AN300_1	0.93	-2.12	0.93	0.71	-3.36	-28.65	14	8	22	57	65
SOH	MINIVOL25	AN300_1	1.01	-3.04	0.91	0.76	-2.86	-24.02	15	11	22	52	65
VCS	MINIVOL25	AN300_1	0.94	-2.66	0.98	0.80	-4.30	-20.21	22	18	26	34	65
	Average		0.96	-2.53	0.95	0.76	-3.22	-24.13	16	15	23	47	
FSF	SFS	AN100	0.85	1.02	0.98	0.97	-3.04	-2.50	37	30	22	12	60
BAC	SFS <sup>d</sup>	AN300_1	0.86	0.94	0.98	0.93	-3.73	-6.80	28	31	20	21	61
	Average		0.85	0.98	0.98	0.95	-3.39	-4.65	33	31	21	17	
FSF	TEOM10	HIVOL10V	0.67	2.17	0.65	0.72	-11.51	-27.52	19	15	16	50	111
BAC	TEOM10	HIVOL10V	0.66	12.55	0.69	0.96	-3.70	-4.19	42	29	9	20	179
LVR1	TEOM10	HIVOL10V	0.74	2.53	0.97	0.88	-2.68	-11.63	44	38	13	6	16
MI 4	TEOM10	HIVOL10V	0.65	5.57	0.73	0.83	-7.40	-16.99	38	20	12	30	118
S13	TEOM10	HIVOL10V	0.70	2.48	0.78	0.81	-6.01	-19.46	35	21	9	35	131
SJ4	TEOM10	HIVOL10V	0.82	1.46	0.96	0.88	-3.59	-11.56	39	41	13	7	56
SOH	TEOM10	HIVOL10V	0.61	6.67	0.74	0.83	-8.02	-17.02	39	19	10	32	113
	Average		0.69	4.77	0.79	0.84	-6.13	-15.48	37	26	12	26	

<sup>a</sup>See Table 1 for site names and Table 2 for sampler descriptions.

<sup>b</sup>R<sup>2</sup> = squared correlation.

<sup>c</sup>Average error:  $AE = 100 \frac{1}{N} \sum_{i=1}^N \frac{Y_i - X_i}{X_i}$

<sup>d</sup>Percent of sample pairs with the absolute value of AE <10%, 10–20%, 20–30%, or >30%.

<sup>e</sup>Five SFS samples from 4/12/00 to 5/6/00 identified in Figure 6 and discussed in the text are excluded.

of a daily Federal PM NAAQS was 1  $\mu\text{g}/\text{m}^3$ . With respect to the Federal 24-hour average PM<sub>2.5</sub> NAAQS (65  $\mu\text{g}/\text{m}^3$ ), no filter-based measurement or comparison between any two samplers is precise enough to resolve that difference.

## CONCLUSIONS

This study indicates that Andersen FRM, RAAS 100 (AN100), and 300 (AN300) samplers perform to standards for FRM equivalence. The difference between FRM samplers was less than 10 and 20% for 70 and 92%, respectively, of the pairwise comparisons. For the other samplers, many of the metrics fall within the U.S. EPA's definition of comparability.  $R^2$  was  $\geq 0.94$  in all cases except for the PM<sub>10</sub> TEOM, which has a FEM designation. The slope was within limits for the BAM25, M1ST, and MINIVOL25 samplers, although the intercepts were not. The SFS, which is a designated PM<sub>10</sub> FRM but not a PM<sub>2.5</sub> FRM, was comparable to the FRM in that results from the two samplers were highly correlated. Parametric statistics imply that most of the PM<sub>2.5</sub> and PM<sub>10</sub> masses from BAM25, DICHOTF, M1ST, MINIVOL25, and SFS differed from those of the FRM. However, in such cases, the differences were comparable to their measurement uncertainties. While some samplers like the PM<sub>2.5</sub> and PM<sub>10</sub> BAM were not equivalent to the FRM, their measurements were highly correlated. Light scattering ( $B_{sp}$ ) measured with the Radiance nephelometer (RAD and RAD25) was also highly correlated with PM<sub>2.5</sub> mass. These continuous measurements can serve as surrogates for 24-h filter-based sample mass with respect to resolving short-term variability and identifying outliers. This was not the case for the PM<sub>2.5</sub> or PM<sub>10</sub> TEOM. The study results suggest that the TEOM is neither equivalent to, nor predictive of, the FRM.

Overall, the comparability among different PM samplers used in CRPAQS is sufficient to evaluate spatial gradients larger than about 15% when the data are pooled together for spatial and temporal analyses. Given that a  $\pm 20\%$  tolerance is suggested for spatial averaging (U.S. EPA 1997c), these differences are sufficient to evaluate sampler zones of representation and to detect spatial gradients. Modeling estimates are not expected to have greater than  $\pm 20\%$  precision. Models are also more effectively tested using the chemical components possible from the non-FRM samplers applied during CRPAQS.

## REFERENCES

- Bevington, P. R., and Robinson, D. K. (1992). *Data Reduction and Error Analysis for the Physical Sciences*. McGraw-Hill, New York, p. 328.
- California Air Resources Board (2002). Draft Proposal to Establish a 24-h Standard for PM<sub>2.5</sub>. Report to the Air Quality Advisory Committee. Public Review Draft, March 12, 2002 ([www.arb.ca.gov/research/aaqs/std-rs/pm25-draft/pm25-draft.htm](http://www.arb.ca.gov/research/aaqs/std-rs/pm25-draft/pm25-draft.htm)).
- Chang, C. T., Tsai, C. J., Lee, C. T., Chang, S. Y., Cheng, M. T., and Chein, H. M. (2001). Differences in PM<sub>10</sub> Concentrations Measured by Beta-Gauge Monitor and Hi-Vol Sampler. *Atmos. Environ.* 35:5741–5748.
- Charron, A., Harrison, R. M., Moorcroft, S., and Booker, J. (2004). Quantitative Interpretation of Divergence Between PM<sub>10</sub> and PM<sub>2.5</sub> Mass Measurement by TEOM and Gravimetric (Partisol) Instruments. *Atmos. Environ.* 38:415–423.
- Chow, J. C., Watson, J. G., Lowenthal, D. H., Solomon, P. A., Magliano, K. L., Ziman, S. D., and Richards, L. W. (1993). PM<sub>10</sub> and PM<sub>2.5</sub> Compositions in California's San Joaquin Valley. *Aerosol Sci. Technol.* 18:105–128.
- Chow, J. C. (1995). Critical Review: Measurement Methods to Determine Compliance with Ambient Air Quality Standards for Suspended Particles. *J. Air & Waste Manage. Assoc.* 45:320–382.
- Chow, J. C., Watson, J. G., Lowenthal, D. H., and Richards, L. W. (2001). Comparability Between PM<sub>2.5</sub> and Particle Light Scattering Measurements. *Environ. Monitor. Assess.* 79:29–45.
- Chow, J. C., Engelbrecht, J. P., Watson, J. G., Wilson, W. E., Frank, N. H., and Zhu, T. (2002). Designing Monitoring Networks to Represent Outdoor Human Exposure. *Chemosphere* 49:961–978.
- Chow, J. C., Watson, J. G., Lowenthal, D. H., and Magliano, K. (2005). Loss of PM<sub>2.5</sub> Nitrate from Filter Samples in Central California. *J. Air & Waste Manage. Assoc.* 55(8):1158–1168.
- Chow, J. C., Watson, J. G., Lowenthal, D. H., Chen, L.-W., and Magliano, K. (2006). Particulate Carbon Measurements in California's San Joaquin Valley. *Chemosphere* 62:337–348.
- Chung, A., Chang, D. P. Y., Kleeman, M. J., Perry, K. D., Cahill, T. A., Dutcher, D., McDougall, E. M., and Stroud, K. (2001). Comparison of Real-Time Instruments used to Monitor Airborne Particulate Matter. *J. Air & Waste Manage. Assoc.* 51:109–120.
- Code of Federal Regulations (1988). *Reference Method for the Determination of Particulate Matter as PM<sub>10</sub> in the Atmosphere*, 40 CFR Part 50, Appendix J. (PM<sub>10</sub> Sampling). U.S. Government Printing Office, Washington, DC., July 1.
- El-Zanan, H. S., Lowenthal, D. H., Zielinska, B., Chow, J. C., and Kumar, N. (2005). Determination of the Organic Aerosol Mass to Organic Carbon Ratio in IMPROVE Samples. *Chemosphere* 60:485–496.
- Hanninen, O. O., Koistinen, K. J., Kousa, A., Keski-Karhu, J., Oyj, S. V., and Jantunen, M. J. (2002). Quantitative Analysis of Environmental Factors in Differential Weighing of Blank Teflon Filters. *J. Air & Waste Manage. Assoc.* 52:134–139.
- Hering, S. V., and Cass, G. R. (1999). The Magnitude of Bias in the Measurement of PM<sub>2.5</sub> Arising from Volatilization of Particulate Nitrate from Teflon Filters. *J. Air & Waste Manage. Assoc.* 49:725–733.
- Keck, L., and Wittmaack, K. (2005). Laboratory Studies on the Retention of Nitric Acid, Hydrochloric Acid and Ammonia on Aerosol Filters. *Atmos. Environ.* 39:2157–2162.
- Lee, J. H., Hopke, P. K., Holsen, T. M., Polissar, A. V., Lee, D.-W., Edgerton, E. S., Ondov, J. M., and Allen, G. (2005). Measurement of Fine Particle Mass Concentrations using Continuous and Integrated Monitors in Eastern U.S. Cities. *Aerosol Sci. Technol.* 39:261–275.
- McDow, S. R., and Huntzicker, J. J. (1990). Vapor Adsorption Artifact in the Sampling of Organic Aerosol: Face Velocity Effects. *Atmos. Environ.* 24A(10):2563–2571.
- Motallebi, N., Taylor, C. A., Jr., Turkiewicz, K., and Croes, B. E. (2003). Particulate Matter in California: Part 1—Intercomparison of Several PM<sub>2.5</sub>, PM<sub>10–2.5</sub>, and PM<sub>10</sub> Monitoring Networks. *J. Air & Waste Manage. Assoc.* 53:1509–1516.
- Peters, T. M., Norris, G. A., Vanderpool, R. W., Gemmill, D. B., Wiener, R. W., Murdoch, R. W., McElroy, F. F., and Pitchford, M. (2001). Field Performance of PM<sub>2.5</sub> Federal Reference Method Samplers. *Aerosol Sci. Technol.* 34:433–443.
- Pang, Y., Eatough, N. L., Wilson, J., and Eatough, D. J. (2002). Effect of Semivolatile Material on PM<sub>2.5</sub> Measurement by the PM<sub>2.5</sub> Federal Reference Method Sampler at Bakersfield, California. *Aerosol Sci. Technol.* 36:289–299.
- Poor, N., Clark, T., Nye, L., Tamanini, T., Tate, K., Stevens, R., and Atkeson, T. (2002). Field Performance of Dichotomous Sequential PM Air Samplers. *Atmos. Environ.* 36:3289–3298.
- Solomon, P. A., Baumann, K., Edgerton, E., Tanner, R., Eatough, D., Modey, W., Maring, H., Savoie, D., Natarajan, S., Meyer, M. B., and Norris, G.

- (2003). Comparison of Integrated Samplers for Mass and Composition During the 1999 Atlanta Supersites Project, *J. Geophys. Res.* 108, D7, 8423, doi:10.1029/2001JD001218.
- Tropp, R. J., Jones, K., Kuhn, G., and Berg, N. J., Jr. (1998). Comparison of PM<sub>2.5</sub> Saturation Samplers with Prototype PM<sub>2.5</sub> Federal Reference Method Samplers. In *Proceedings, PM<sub>2.5</sub>: A Fine Particle Standard*, Chow, J. C., and Koutrakis, P., Eds. Air & Waste Management Association, Pittsburgh, PA, p. 215–225.
- U.S. Environmental Protection Agency (U.S. EPA) (1987). Revisions to the National Ambient Air Quality Standards for Particulate Matter: 40 CFR Part 50, *Federal Register* 52:24634.
- U.S. Environmental Protection Agency (U.S. EPA) (1997a). National Ambient Air Quality Standards for Particulate Matter: Final Rule. 40 CFR Part 50, *Federal Register* 62(138):38,651–38,701.
- U.S. Environmental Protection Agency (U.S. EPA) (1997b). Revised Requirements for Designation of Reference and Equivalent Methods for PM<sub>2.5</sub> and Ambient Air Quality Surveillance for Particulate Matter: Final Rule. 40 CFR Parts 53 and 58, *Federal Register* 62(138):38,763–38,854.
- U.S. Environmental Protection Agency (U.S. EPA) (1997c). Guidance for Network Design and Optimum Site Exposure for PM<sub>2.5</sub> and PM<sub>10</sub>. Report No. EPA-454/R-99-022. Research Triangle Park, NC (<http://www.epa.gov/ttnamti1/files/ambient/pm25/network/r-99-022.pdf>)
- Watson, J. G., Chow, J. C., Shah, J. J., and Pace, T. G. (1983). The Effect of Sampling Inlets on the PM<sub>10</sub> and PM<sub>15</sub> to TSP Concentration Ratios, *J. Air Poll. Control Assoc.* 33:114–119.
- Watson, J. G., Cooper, J. A., and Huntzicker, J. J. (1984). The Effective Variance Weighting for Least Squares Calculations Applied to the Mass Balance Receptor Model, *Atmos. Environ.* 18:1347–1355.
- Watson, J. G., DuBois, D. W., DeMandel, R., Kaduwela, A., Magliano, K., McDade, C., Mueller, P. K., Ranzieri, A., Roth, P. M., and Tanrikulu, S. (1998). Aerometric Monitoring Program Plan for the California Regional PM<sub>10</sub>/PM<sub>2.5</sub> Air Quality Study; Prepared for the California Regional PM<sub>10</sub>/PM<sub>2.5</sub> Air Quality Study Technical Committee, Sacramento, CA, by the Desert Research Institute, Reno, NV, December 20, 1998. (<http://www.arb.ca.gov/airways/crpaqs/publications.htm>)
- Watson, J. G., Chow, J. C., Bowen, J. L., Lowenthal, D. H., Hering, S., Ouchida, P., and Oslund, W. (2000). Air Quality Measurements from the Fresno Supersite, *J. Air & Waste Manage. Assoc.* 50:1321–1334.
- Watson, J. G., and Chow, J. C. (2002). Comparison and Evaluation of In Situ and Filter Carbon Measurements at the Fresno Supersite, *J. Geophys. Res.* 107, D21.
- Wedding, J. B., and Carney, T. C. (1983). A Quantitative Technique for Determining the Impact of Non-Ideal Ambient Sampler Inlets on the Collected Mass, *Atmos. Environ.* 17:873–882.